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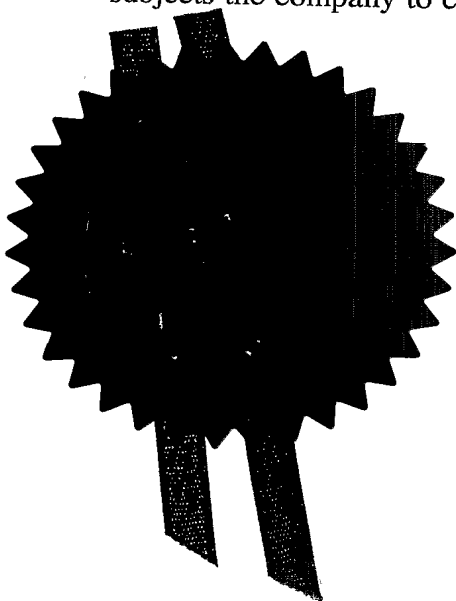
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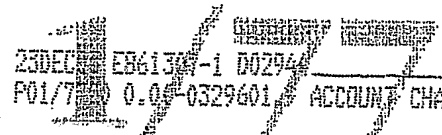
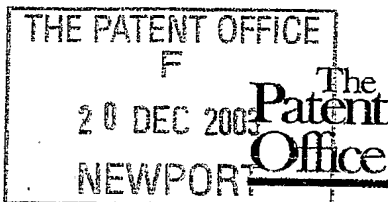


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1. Your reference SMC 60642/GB/P1

2. Patent application number ~~20 DEC 2003~~
(The Patent Office will fill in this part) 0329601.9

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

Avecia Limited
Hexagon House
Blackley
Manchester, M9 8ZS
United Kingdom
07764137001

GB

4. Title of the invention PROCESS

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

MAYALL, John

Avecia Limited
Hexagon House
Blackley
Manchester, M9 8ZS
United Kingdom

Patents ADP number (if you know it) 6244313002 7764137003

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

| Country | Priority application number (if you know it) | Date of filing (day / month / year) |
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| Number of earlier application | Date of filing (day / month / year) |
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16

Claim(s)

03

Abstract

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Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

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Request for substantive examination (*Patents Form 10/77*)

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11.

I/We request the grant of a patent on the basis of this application.

Signature

C. Shepherd

Date

19/12/03

Avecia Limited Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

Mrs K.M. Pinder/Mrs G. Shepherd 0161 721 1361/2

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SMC 60642



APPLICANTS

AVECIA LIMITED

TITLE

PROCESS

PROCESS

This invention relates to a process for preparing encapsulated particulate solids and to paints, mill-bases and inks (especially ink jet printing inks) containing such solids.

5 Many inks, mill-bases, paints and the like require effective dispersants for uniformly distributing a particulate solid in a liquid vehicle. The liquid vehicle may vary from highly polar (e.g. water) to highly non-polar (e.g. toluene). Known dispersants tend to work effectively only with liquid vehicles within a range of polarities. Outside such polarities the particulate solid typically flocculates. Thus a range of dispersants has been developed for liquid vehicles of different polarities.

10 Conventional dispersants suffer from a disadvantage in that they may readily be displaced from the surface of a particulate solid by a more strongly absorbing material. This can result in destabilisation and flocculation of the solid from dispersions containing it.

15 The problems associated with conventional dispersants can be addressed in part by encapsulating a particulate solid within a cross-linked dispersant. The process of encapsulation is typically performed in a liquid medium. A cross-linkable dispersant can be mixed with a particulate solid distributed in a liquid medium, the dispersant then absorbs onto the particulate solid surface and the dispersant is then cross-linked via its cross-linkable groups by means of a cross-linking agent to encapsulate the particulate
20 solid within the cross-linked dispersant. Such an approach is described in US 6262152, WO 0020520, JP 199710483, JP 1999152424 and EP 732381.

We have found encapsulation process approaches described in the prior art often suffer from significant deficiencies. For example, US 6,262,152 and WO0020520 describe media-insoluble cross-linking agents which are difficult to dissipate into the liquid medium
25 and tend to cause flocculation of the particulate solid during addition of the cross-linking agent and/or during the cross-linking reaction.

In JP1999152424 and JP199710483 the initial dispersants used prior to cross-linking are relatively hydrophobic. This results in poor wetting and milling of the pigment used and requires an organic solvent to fully dissolve the dispersant. The resulting
30 encapsulated pigment has relatively large particle size and exhibits poor stability. EP 732381 describes a hydrophobic urethane cross-linking composition which is delivered with a colorant and an organic solvent into an aqueous medium. Such hydrophobic cross-linking compositions result in hydrophobic in-situ dispersants which give rise to relatively coarse and less stable dispersions.

35 The hydrophobicity of a dispersant can be characterised by its Log P value. Log P is the logarithm (base 10) of the partitioning co-efficient of a substance between n-octanol and water as described in L. G. Danielsson and Y. H. Zhang, Trends in Anal. Chem., 1996, 15, 188. High Log P values signify hydrophobic compounds (e.g. Styrene Log P approximately 3) and low Log P values signify hydrophilic compounds (e.g. Acrylic acid

Log P approximately 0). Log P values can be calculated which are in good agreement with experimental determinations (Analytical Sciences Sept 2002, Vol 18, pages 1015 to 1020). Calculated Log P values are preferred, however, since commercial computer programmes exist which can accurately and quickly calculate the Log P values of large numbers of real or hypothetical compounds .

According to a first aspect of the present invention there is provided a process for preparing an encapsulated, particulate solid comprising cross-linking a poly vinyl dispersant with a cross-linking agent in the presence of a particulate solid and a liquid medium, thereby encapsulating the particulate solid within the cross-linked poly vinyl dispersant, characterised in that:

- a) the poly vinyl dispersant has a calculated Log P of less than 1.8 and at least one cross-linkable group; and
- b) the cross-linking agent is soluble in the liquid medium and has at least one cross-linking group.

ENCAPSULATED PARTICULATE SOLID

Preferably the process is performed such that the cross-linked dispersant encapsulates single particulate solid particles. Some of the particulate solid will tend to exist as clusters thus accordingly some of the encapsulated particulate solid particles will exist as cross-linked dispersant encapsulating a plurality of particulate solid particles, although it is preferred that most or substantially all of the encapsulated particles contain only one particle of particulate solid.

PARTICULATE SOLID

The particulate solid may be any inorganic or organic particulate solid or a mixture of such solids thereof which is at least partially insoluble in the liquid medium. Preferably the particulate solid is a colorant, more preferably a pigment .

Examples of suitable particulate solids are inorganic and organic pigments, extenders, fillers for paints and plastics materials; disperse dyes and water-soluble dyes in liquid media which do not fully dissolve said dyes; optical brightening agents; textile auxiliaries for solvent dyebaths, inks and other solvent application system; solids for oil-based and inverse-emulsion drilling muds; particulate ceramic materials; and magnetic particles (e.g. for use in magnetic recording media); biocides; agrochemicals; and pharmaceuticals.

A preferred particulate solid is an organic pigment, for example any of the pigments described in the Third Edition of the Colour Index (1971) and subsequent revisions of, and supplements thereto, under the chapter headed "Pigments". Examples of organic pigments are those from the azo (including disazo and condensed azo), thioindigo, indanthrone, isoindanthrone, anthanthrone, anthraquinone, isodibenzanthrone, triphenyldioxazine, quinacridone and phthalocyanine series, especially copper

phthalocyanine and its nuclear halogenated derivatives, and also lakes of acid, basic and mordant dyes. Carbon black, although often regarded as being inorganic, behaves more like an organic pigment in its dispersing properties and is another example of a suitable particulate solid. Preferred organic pigments are phthalocyanines, especially copper phthalocyanine pigments, azo pigments, indanthrones, anthranthrones, quinacridones and carbon black pigments.

Preferred inorganic particulate solids include: extenders and fillers, e.g. talc, kaolin, silica, barytes and chalk; particulate ceramic materials, e.g. alumina, silica, zirconia, titania, silicon nitride, boron nitride, silicon carbide, boron carbide, mixed silicon-aluminium nitrides and metal titanates; particulate magnetic materials e.g. magnetic oxides of transition metals, especially iron and chromium, e.g. $\gamma\text{-Fe}_2\text{O}_3$, Fe_3O_4 , and cobalt-doped iron oxides, calcium oxide, ferrites, especially barium ferrites; and metal particles, especially metallic iron, nickel, cobalt and alloys thereof.

Where the process of the present invention is used to make encapsulated particulate solids for use in ink jet inks the pigment is preferably a cyan, magenta, yellow or black pigment.

LIQUID MEDIUM

The liquid medium may be non-polar but is preferably polar. "Polar" liquids are generally capable of forming moderate to strong intra-molecular bonds, e.g. as described in the article entitled "A Three Dimensional Approach to Solubility" by Crowley et al in Journal of Paint Technology, Vol. 38, 1966, at page 269. Polar liquid media generally have a hydrogen bonding number of 5 or more as defined in the abovementioned article.

Examples of suitable polar liquid media include ethers, glycols, alcohols, amides and especially water. Numerous specific examples of polar liquid media are given in the book entitled "Compatibility and Solubility" by Ibert Mellan (published in 1968 by Noyes Development Corporation) in Table 2.14 on pages 39-40, which is incorporated herein by reference thereto.

Preferred polar liquid media contain up to, and including, a total of 6, 7 or 8 carbon atoms, especially C_{1-6} -alkanols. As examples of the preferred polar liquid media there may be mentioned glycols and glycol esters and ethers, e.g. ethylene glycol, 2-ethoxyethanol, 3-methoxypropylpropanol, 3-ethoxypropylpropanol; alkanols, e.g. methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol and isobutanol; cyclic ethers and amides, especially cyclic amides, e.g. pyrrolidone and *n*-methyl pyrrolidone; more especially water; and combinations thereof.

The polar liquid medium is optionally a polyol, that is to say, a liquid with two or more hydroxy groups. Preferred polyols include glycerol, alpha-omega diols and especially alpha-omega diol ethoxylates.

Preferably the liquid medium comprises water as this tends to result in a particularly stable and fine encapsulated particulate solid. Preferably the liquid medium

comprises from 1 to 100%, more preferably from 10 to 100%, especially from 20 to 90% and more especially from 30 to 80% water by weight.

Preferred non-polar liquid media include non-halogenated aromatic hydrocarbons (e.g. toluene and xylene); halogenated aromatic hydrocarbons (e.g. chlorobenzene, dichlorobenzene and chlorotoluene); non-halogenated aliphatic hydrocarbons (e.g. linear and branched aliphatic hydrocarbons containing six or more carbon atoms, including fully and partially saturated), halogenated aliphatic hydrocarbons (e.g. dichloromethane, carbon tetrachloride, chloroform, trichloroethane); natural non-polar liquids (e.g. vegetable oil, sunflower oil, linseed oil, terpenes and glycerides); and combinations thereof.

The liquid medium may comprise a mixture of liquids which may be polar or non-polar liquids. It is preferred that at least one component of the liquid medium is a polar liquid.

Preferably the liquid medium is not reactive towards either the cross-linking agent or the dispersant, e.g. the cross-linking agent and dispersant react with each other more quickly than they react with the liquid medium or any component thereof. Thus for example where the cross-linking agent is an isocyanate the liquid medium preferably contains no groups which are reactive with an isocyanate such as amine, thiol and hydroxyl groups (unreactive and low reactive amine, thiol and hydroxy groups being acceptable).

CROSS-LINKING AGENT

The cross-linking agent is preferably soluble in the liquid medium. The cross-linking agent need not be 100% soluble in the liquid medium, for example a small percentage (for example less than 1% by weight of the total cross-linking agent) of the cross-linking agent may be insoluble in the liquid medium.

Soluble cross-linking agents are distinguished from media insoluble cross-linking agents as described in US 6262152 and WO 00/20520, which must be dispersed in a liquid medium using a surfactant or dispersant.

The cross-linking group(s) in the cross-linking agent and the cross-linkable group(s) in the poly vinyl dispersant are chosen as a co-reactive pair. Table 1 indicates preferred pairs of cross-linking and cross-linkable groups.

TABLE 1

| Cross-linkable group in the poly vinyl dispersant | Cross-linking groups in the cross-linking agent |
|---|---|
| Epoxy | Amine, anhydride, thiol, acid, hydrazide, phenolic, N-alkylol. |
| Hydroxy / thiol | Isocyanates, epoxy, anhydride, acid, N-alkoyl, carbodiimide, aziridine. |
| Anhydride, acid chloride, carboxylic acid | Epoxy, amine, hydroxy, isocyanate, aziridine, carbodiimide, thiol. |
| aldehyde, keto, beta-diketoester | Amine, imine, thiol, hydrazide, activate olefin, diazonium, carbonyl containing. |
| Activated olefinic bond | Amine, thiol, radical initiator, dienes (Diels-alder reactive), enolate anions. |
| Amine / Hydrazine / Imine / thiol | Epoxy, isocyanate, aldehyde, ketone beta-diketoester, activated olefinic bond, N-alkoyl. |
| Silane, halosilane, alkoxy silane, acetosilane, silicate, silanol | Hydroxy, acid, isocyanate, silane, halosilane, alkoxy silane, acetosilane, silicate, silanol. |
| Vinyls especially, (meth) acrylates | Vinyls especially, (meth) acrylates used with an initiator, redox initiator, photoinitiator, free radical initiator |
| Electrophiles, Freidel Krafts agents, diazonium. | Aromatic groups |

5 Preferably pairs of cross-linking and cross-linkable groups are used as indicated across the rows of Table 1 but it will be readily apparent that the cross-linking groups on the cross-linking agent can be interchanged with the cross-linkable groups on the poly vinyl dispersant.

10 Particularly preferred cross-linking groups are activated olefins, diazonium and carbonyl containing groups and especially amine, imine, hydrazide and thiol groups. Amine, imine, hydrazide and thiol groups cross-linking groups are preferably paired with keto, aldehyde and especially beta-diketoester dispersant cross-linkable groups. Such pairing of cross-linkable and cross-linking groups is preferred as milder cross-linking conditions are facilitated.

The cross-linking agent must have at least one cross-linking group which is reactive towards the cross-linkable group(s) on the dispersant. In order that a single group can cross-link it should be such that it can bond to two or more poly vinyl dispersant cross-linkable groups. Preferred examples of cross-linking groups which can form two or more bonds per group are unsaturated groups such as aromatic groups (e.g. those containing the residues of benzene, naphthalene and the like), ethylenic groups, and acetylenic groups. Especially preferred are vinyl groups and more especially (meth) acrylate groups.

The vinyl groups in the poly vinyl dispersant are preferably (meth) acrylate groups and the cross-linking agent preferably also has one or more vinyl groups which are preferably (meth) acrylate groups, and the cross-linking is preferably facilitated by the presence of an initiator in the liquid medium. Preferably the initiator is a free radical initiator.

The cross-linking agent preferably has two or more cross-linking groups. These groups may be the same or different. Preferred cross-linking agents have from two to ten cross-linking groups. Two or more cross-linking agents can be used. In such case these may have a different number of cross-linking groups and/or may use different types of cross-linking groups.

POLY VINYL DISPERSANT

Preferred poly vinyl dispersants are poly styrenics, poly (meth) acrylates and copolymers comprising one or both thereof.

Preferably the poly vinyl dispersant has a number average molecular weight of from 500 to 100,000, more preferably from 1,000 to 50,000 and especially from 1,000 to 35,000.

Preferred poly vinyl dispersants comprise both hydrophilic and hydrophobic monomers.

The poly vinyl dispersants are preferably random (e.g. having statistically short blocks or segments) but can be alternating, block, graft or star (e.g. having longer blocks or segments). Poly vinyl dispersants can be branched or star but are preferably linear. Poly vinyl dispersants may have two or more segments but are preferably random.

In embodiments where the poly vinyl dispersant has two or more segments it is preferred that at least one segment is hydrophobic and at least one segment is hydrophilic relative to each other. A preferred method for making hydrophilic and hydrophobic segments is by the polymerisation of hydrophilic and hydrophobic monomers respectively. Where the dispersant has at least one hydrophilic and at least one hydrophobic segment the cross-linkable group can be situated in a hydrophobic segment, in a hydrophilic segment or in both.

Hydrophilic monomers are those monomers comprising hydrophilic groups which may be ionic or non-ionic groups. The ionic groups may be cationic but are preferably

anionic. Both cationic and anionic groups may be used to give an amphoteric poly vinyl dispersant. Preferred anionic groups are phenoxy, carboxylic acid, sulphonic acid and phosphoric acid groups which may be in the free acid or salt form. Preferred salts forms are ammonium, substituted ammonium, quaternary ammonium, sodium, lithium and potassium salts.

Preferred cationic groups are substituted ammonium, quaternary ammonium, benzalkonium, guanidine, biguanidine and pyridinium. These can be in the form of a free base or a salt (e.g. a hydroxide, sulphate, nitrate, chloride, bromide, iodide or fluoride salt or in the form of a quaternary ammonium salt formed with for example an alkyl halide or dimethyl sulphate).

Preferred non-ionic groups are glucosides, saccharides, pyrrolidone, acrylamide residues and especially alkyleneoxy (e.g. propyleneoxy, ethyleneoxy and combinations thereof) and hydroxy groups. The poly vinyl dispersant can contain a single non-ionic group, several non-ionic groups throughout the dispersant or one or more polymeric chains containing non-ionic groups. Hydroxy groups can be incorporated using polymeric chains such as polyvinylalcohol, polyhydroxyl functional acrylics and celluloses. Alkyleneoxy groups can be incorporated using polymeric chains such as polyethyleneoxide, polypropyleneoxide and polyethyleneoxide-co-polypropyleneoxide.

Hydrophobic monomers are those monomers comprising hydrophobic groups. Preferred hydrophobic groups are predominantly hydrocarbons, fluorocarbons and alkyl siloxanes comprising less than three and more preferably no hydrophilic groups. The hydrophobic group is preferably a C_{3-50} chain which can be pendant or in chain with the hydrophobic monomer.

Poly vinyl dispersants may be made by any means known in the art. A preferred method for making poly vinyl dispersants is free radical polymerisation of vinyl monomers, especially (meth)acrylates, vinyl monomer containing aromatic groups such as vinyl naphthalene and styrenic monomers. Suitable free radical polymerisation methods include but are not limited to suspension, solution, dispersion and preferably emulsion polymerisation.

Poly vinyl dispersants which contain the residue of both hydrophilic and hydrophobic monomers can be made essentially without segments. Using cost effective, conventional and robust free radical polymerisation methods the segment length is often statistically very short or effectively non-existent. This is the case in what are often referred to as "random" polymerisations. Thus in order to produce less preferred segment structures with longer segment lengths more exotic and more costly polymerisation methods such as living polymerisations and especially group transfer polymerisation, atom transfer polymerisation, macromonomer polymerisation, graft polymerisation and anionic or cationic polymerisation are required.

Suitable hydrophilic vinyl monomers include non-ionic and ionic monomers.

Preferred non-ionic vinyl monomers are those containing saccharide, glucoside, amide, pyrrolidone and especially hydroxy and ethoxy groups.

Preferred examples of non-ionic vinyl monomers include hydroxy ethylacrylate, hydroxy ethyl methacrylate, vinyl pyrrolidone, ethoxylated (meth)acrylates, (meth)acrylamides and ethylenoxy-propyleneoxy functional (meth)acrylates.

The ionic vinyl monomer may be cationic but is preferably anionic. Preferred anionic vinyl monomers are those comprising phosphoric acid groups, sulphonic acid groups and especially carboxylic acid groups which may be in the free acid (protonated) form or salt form. The salts are as described hereinbefore. Preferred examples are acrylic acid, methacrylic acid, itaconic acid, β -carboxy ethyl acrylate, maleic acid, monoalkyl itaconates (for example, monomethyl maleate, monoethyl maleate, monobutyl maleate and monooctyl maleate), citraconic acid, styrenesulfonic acid, vinylbenzylsulfonic acid, vinylsulfonic acid, acryloyloxyalkyl sulfonic acids (for example, acryloyloxymethyl sulfonic acid, acryloyloxyethyl sulfonic acid, acryloyloxypropyl sulfonic acid and acryloyloxybutyl sulfonic acid), methacryloyloxymethyl sulfonic acid, methacryloyloxyethyl sulfonic acid, methacryloyloxypropyl sulfonic acid and methacryloyloxybutyl sulfonic acid), 2-acrylamido-2-alkylalkane sulfonic acids (for example, 2-acrylamido-2-methylethanesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid and 2-acrylamido-2-methylbutane sulfonic acid), 2-methacrylamido-2-alkylalkane sulfonic acids (for example, 2-methacrylamido-2-methylethanesulfonic acid, 2-methacrylamido-2-methylpropanesulfonic acid and 2-methacrylamido-2-methylbutanesulfonic acid), mono-(acryloyloxyalkyl)phosphates (for example, mono(acryloyloxyethyl)phosphate and mono(3-acryloyloxypropyl)phosphates) and mono(methacryloyloxyalkyl)phosphates (for example, mono(methacryloyloxyethyl)phosphate and mono(3-methacryloyloxypropyl)phosphate).

Especially preferred vinyl anionic monomers are acrylic acid, itaconic acid, β -carboxy ethyl acrylate, maleic acid and most especially methacrylic acid.

Preferred cationic monomers are those comprising substituted amine, quaternary amine, pyridine, guanidine and/or biguanidine groups. Especially preferred cationic acrylic monomers include dimethyl amino ethyl (meth)acrylate, diethyl amino ethyl (meth)acrylate, vinyl pyridine, dimethyl amino propyl methacrylamide and dimethyl amino butyl acrylate. These can be in the form of the free base (unprotonated), in the form of salt or in the form of a quaternary ammonium salt.

Preferred hydrophobic vinyl monomers have no hydrophilic groups. Preferred hydrophobic vinyl monomers include C_{1-20} -hydrocarbyl (meth)acrylates, butadiene, styrene and vinyl naphthalene. Especially preferred C_{1-20} -hydrocarbyl (meth)acrylates are butyl (meth)acrylate, octyl (meth)acrylate, 2-ethyl hexyl (meth) acrylate, isobornyl acrylate, lauryl acrylate and stearyl acrylate.

CALCULATED LOG P

The calculated Log P of a dispersant may be calculated using commercially available computer software, for example using the Log P DB software version 7.04 or a later version of such software (which is available from Advanced Chemistry Development Inc (ACD labs)). Any ionic or ionisable groups are calculated in their neutral (unionised) form. For poly vinyl dispersants the calculated Log P may be derived from a weight contribution equation (1) based on its monomer components:

$$\text{calculated Log P (polymeric dispersant)} = \sum[W(i) \times \text{calc Log P}(i)]$$

Equation (1)

wherein W(i) is the weight fraction of monomer (i) based on the total weight of poly vinyl dispersant and calc Log P(i) is the calculated Log P of that monomer.

Calculated Log Ps of monomers are well known in the art, for example as described in Table 2:

TABLE 2

| Monomer component of the dispersant | ACD labs Log P DB |
|-------------------------------------|-------------------|
| Acrylic acid (neutral form) | 0.28 |
| Methacrylic acid (neutral form) | 0.83 |
| Methyl methacrylate | 1.35 |
| Acetoacetoxy ethyl methacrylate | 1.62 |
| 2-Ethyl hexyl acrylate | 4.33 |
| 2-Hydroxy ethyl acrylate | -0.05 |
| n-Butyl acrylate | 2.39 |
| Dimethyl amino ethylmethacrylate | 1.50 |
| 2-ethyl hexyl methacrylate | 4.88 |
| 2-hydroxy ethyl methacrylate | 0.50 |
| Glycidyl methacrylate | 1.39 |
| Styrene | 2.70 |
| n-Butyl methacrylate | 2.94 |

Table 2 lists preferred monomeric components of poly vinyl dispersants and their associated calculated Log P values. Thus by example, a dispersant comprising 40% by weight styrene residues and 60% by weight 2-hydroxy ethyl acrylate residues has a calculated Log P value of $[(0.4 \times 2.70) + (0.6 \times -0.05)]$ which is 1.05.

The poly vinyl dispersant preferably has a calculated Log P of not less than 0. Very hydrophilic poly vinyl dispersants tend not to adsorb well onto a particulate solid and are

less effective in milling and stabilising the particulate solid in the liquid medium. Hence a preferred poly vinyl dispersant has a calculated Log P of from 0 to 1.8, more preferably from 0 to 1.7 and especially from 1 to 1.65.

5 The poly vinyl dispersant must have at least one cross-linkable group but more preferably has two or more cross-linkable groups. The cross-linkable groups may be the same or different. Higher numbers of cross-linkable groups promote faster and more effective cross-linking.

10 Preferred cross-linkable group or groups in the poly vinyl dispersant are as indicated in Table 1, column 1. It is, of course, perfectly possible to interchange the dispersant cross-linkable group with the cross-linking agent cross-linking group. Preferred co-reactive pairs of poly vinyl dispersant cross-linkable group and cross-linking agent cross-linking group are as hereinbefore described in Table 1.

15 The cross-linkable group in the poly vinyl dispersant is preferable incorporated by means of polymerising or copolymerising a vinyl monomer comprising the cross-linkable group.

Many vinyl monomers with cross-linkable groups are commercially available, for example, from the PolySciences Inc catalogue 2002-2003, pages 212 to 213.

20 Preferred cross-linkable groups are keto, aldehyde and especially a beta-diketoester groups. The cross-linkable group or groups are preferably incorporated by means of a keto, aldehyde or beta-diketoester functional vinyl monomer which is then polymerised with other vinyl monomers to give the poly vinyl dispersant.

25 Preferred vinyl monomers containing at least one keto, aldehyde or beta-diketoester group are acrolein, methyl vinyl ketone, diacetone acrylamide and especially acetoacetoxy ethylmethacrylate. Hence preferred poly vinyl dispersants comprise at least one residue of such monomers

30 Preferably the vinyl monomer containing at least one keto, aldehyde or beta-diketoester group is incorporated at from 80 to 0.1 mole%, more preferably from 70 to 5 mole% and especially from 70 to 10 mole% based on all the monomers used to make the dispersant.

The acid value (AV) of the poly vinyl dispersant is preferably from 10 to 200, more preferably from 30 to 150 and especially from 60 to 120mg KOH / g of the dispersant.

More than one type of poly vinyl dispersant may be used.

35 The poly vinyl dispersant need not be totally soluble in the liquid medium. That is to say perfectly clear and non-scattering solutions are not essential. The poly vinyl dispersant may aggregate in surfactant-like micelles giving slightly hazy solutions in the liquid medium. Further the poly vinyl dispersant may be such that some proportion of the dispersant tends to form a colloid or particulate dispersion. It is preferred that the poly vinyl dispersant produces uniform and stable dispersions in the liquid medium which do not settle or separate on standing.

It is preferred that the poly vinyl dispersant produces uniform and stable dispersions in the liquid medium which do not settle or separate on standing.

It is preferred that the poly vinyl dispersant is substantially soluble in the liquid medium giving rise to clear or hazy solutions.

5 Preferred poly vinyl dispersants are random and tend to give clear compositions whilst less preferred dispersants with two or more segments tend to give rise to the aforementioned hazy compositions in liquid media.

10 The poly vinyl dispersant is preferably chosen to suit the liquid medium to be used in the process for preparing the encapsulated particulate solid and optionally also any liquid vehicle to be used in the final intended composition in which the encapsulated particulate solid will be used (e.g. an ink or paint). Thus, for example, where the encapsulated particulate solid is to be used in an aqueous ink jet ink the poly vinyl dispersant preferably has a predominantly hydrophilic character. Similarly where the encapsulated particulate solid is to be used in an oil-based paint or ink the poly vinyl dispersant preferably has a predominantly hydrophobic character.

PROCESS PREFERENCES

20 Preferably the cross-linking is performed by mixing the particulate solid, the poly vinyl dispersant, the cross-linking agent and the liquid medium. Preferably the weight ratio of the particulate solid to liquid medium is from 1:100 to 1:2.5, more preferably 1:100 to 1:3, especially 1:100 to 1:5. Preferably the weight ratio of the poly vinyl dispersant to the liquid medium is 1:1000 to 1:2.5, more preferably 1:100 to 1:3.3, especially 1:100 to 1:5. Preferably the cross-linking agent is present in the liquid medium at a concentration such that the molar ratio of cross-linking groups in the cross-linking agent to the cross-linkable groups in the poly vinyl dispersant is from 10:1 to 1:10, more preferably from 1:5 to 5:1 and especially from 1:2 to 1:2. This typically equates a weight ratio of cross-linking agent to liquid medium of 1:10000 to 1:10, more preferably 1:2000 to 1:20.

Thus preferably the cross-linking is performed by mixing the following ingredients:

- a) the liquid medium;
- 30 b) the particulate solid in a weight ratio of 1:100 to 1:3, more preferably 1:100 to 1:5;
- c) the poly vinyl dispersant in a weight ratio of 1:100 to 1:3.3, more preferably 1:100 to 1:5; and
- d) the cross-linking agent in a weight ratio of 1:10000 to 1:10; more preferably 1:2000 to 1:20;

35 wherein all weight ratios are relative to the weight of the liquid medium.

The mixing may be performed by any method, e.g. mechanical agitation, stirring and so on. Low temperatures for cross-linking are preferred as this results in lower levels of flocculation and particle size growth of the particulate solid in the liquid medium.

40 Preferably the cross-linking is performed at a temperature of less than 100°C, more

preferably less than 80°C, especially less than 60°C, more especially at less than 40°C. The lower temperature limit for cross-linking is determined by the freezing point of the liquid medium and the desired rate of reaction but a preferred lower limit is 0°C.

The time for the cross-linking depends to some extent on the temperature and presence or absence of a catalyst. However a preferred time is from 1 to 24 hours, more preferable from 1 to 8 hours. If desired a catalyst may be added to speed up the reaction.

The particulate solid, the liquid medium and the poly vinyl dispersant may be mixed in any order or simultaneously. The mixture is optionally subjected to a mechanical treatment to reduce the particle size of the solid to a desired size, for example by ball milling, bead milling, gravel milling or by more elaborate techniques such as microfluidizing (using a Microfluidics™ machine) or using hydrodynamic cavitation (using for example the CaviPro™ device) until the desired particle size is achieved. Alternatively, the particulate solid may be treated to reduce its particle size independently or in admixture with either the liquid medium or the poly vinyl dispersant, the other ingredient or ingredients then being added and the mixture being agitated to provide the dispersion.

If desired the dispersion may be filtered or centrifuged to remove any poorly dispersed or over-sized particulate material prior to cross-linking. In particular the process preferably comprises filtering a mixture comprising the poly vinyl dispersant, a particulate solid and liquid medium prior to cross-linking, preferably through a filter having a pore size of less than 10, more preferably less than 5 and especially less than 1 micron.

If the cross-linking agent is present during mechanical treatment of the particulate solid this can result in undesirable pre-cross-linking of the dispersion before the particle size of the solid has been fully reduced. When the particulate solid is milled in the presence of the poly vinyl dispersant and the liquid medium the temperature is preferably not greater than 40°C and especially not greater than 30°C.

The cross-linking agent is preferably added to a mixture comprising the particulate solid, poly vinyl dispersant and liquid medium after mechanical treatment to reduce the particle size of the particulate solid. Cross-linking can occur whilst the cross-linking agent is being added but it is more preferred that most of the cross-linking occurs after complete addition of the cross-linking agent. It is also preferred that less than 10% cross-linking has occurred 30 minutes after the complete addition of the cross-linking agent. This facilitates more uniform dispersion of the cross-linking agent throughout the composition and results in more uniform cross-linking.

To delay cross-linking until the cross-linking agent has been added to a mixture comprising the particulate solid, poly vinyl dispersant and liquid medium the cross-linking agent is preferably added to said mixture at a temperature below 60°C and especially below 30°C. Also it is preferred that where the process uses a catalyst to increase the speed of crosslinking this is added after the addition of the cross-linker.

The process preferably results in an encapsulated particulate solid having a volume average particle size of at most 50% greater than the volume average particle size of the particulate solid prior to addition of the cross-linking agent.

5 Preferably the encapsulated particulate solid has a volume average particle size of less than 300nm, more preferably from 10 to 300nm, because such particles are particularly useful in paints, inks and especially in ink jet printing inks.

The volume average particle size may be measured by any means known but a preferred method is via photo correlation spectroscopy techniques as available from MalvernTM and CoulterTM.

10 ENCAPSULATED SOLID

If desired the process may further comprise the step of isolating the resultant encapsulated particulate solid from the liquid medium. This may be achieved by, for example, evaporating the liquid medium, or by precipitation or flocculation of the
15 encapsulated particulate solid followed by filtration.

Preferred methods of evaporation include freeze drying, spray drying and agitated drying. Preferred methods of precipitation and flocculation include the addition of metal salts, freeze/thawing and centrifugation.

20 According to a second aspect of the present invention there is provided an encapsulated particulate solid obtainable or obtained by the process of the first aspect of the present invention.

COMPOSITIONS AND INKS

25 The encapsulated particulate solid prepared by the process of the present invention is useful in the manufacture of compositions comprising the encapsulated particulate solid and a liquid vehicle. Preferably such compositions are inks and the particulate solid is a colorant, especially a pigment.

30 Thus according to a third aspect of the present invention there is provided a composition comprising a liquid vehicle and an encapsulated particulate solid obtained or obtainable by a process according to the first aspect of the present invention.

35 The compositions may be prepared by diluting the product of the process, or by isolating the product of the process and mixing the isolated encapsulated particulate solid with a liquid vehicle. It is preferable to prepare the composition by adding desired liquid vehicle components to the composition comprising the encapsulated particulate solid and the liquid medium resulting from the process according to the first aspect of the present invention. This process, which does not isolate the encapsulated particulate solid, tends to result in smaller particle size of the encapsulated particulate solid.

THE LIQUID VEHICLE

The liquid vehicle may be identical to or different from the liquid medium used in the process for preparing the encapsulate solid. It is often desirable that the liquid vehicle comprises high proportions of water and that further liquids required to make the desired composition (e.g. an ink) are added after the process according to the first aspect of the present invention.

The liquid medium is preferably an organic solvent, water or a mixture comprising an organic solvent and water.

Preferably the liquid vehicle comprises water, especially when the compositions are intended for use in ink jet printing. Preferably the liquid vehicle comprises from 50 to 95%, more preferably from 60 to 95% and especially from 60 to 90% water by weight based on the total weight of the composition.

In the case of ink jet printing compositions it is preferable that the liquid vehicle comprises both water and an organic solvent which is preferably a water-miscible organic solvent. Preferred water-miscible organic solvents for inclusion into the liquid vehicle include C_{1-6} -alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono- C_{1-4} -alkyl ethers of diols, preferably mono- C_{1-4} -alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy) ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone. Preferably the liquid vehicle comprises water and 2 or more, especially from 2 to 8, water-miscible organic solvents.

Especially preferred water-miscible organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C_{1-4} -alkyl and C_{1-4} -alkyl ethers of diols, more preferably mono- C_{1-4} -alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol; and glycerol.

A preferred composition comprises:

- a) from 0.1 to 50 parts, more preferably from 1 to 25 parts, of an encapsulated particulate solid obtainable or obtained by a process according to the first aspect of the present invention; and
- b) from 50 to 99.9 parts, more preferably from 99 to 75 parts, of a liquid vehicle comprising water, an organic solvent or both water or an organic solvent;

wherein all parts are by weight and the amount of components a) and b) add to 100 parts.

The weight ratio of water to organic solvent when both are present in the liquid vehicle is preferably in the range 99:1 to 5:95, more preferably 95:5 to 60:40, especially 95:5 to 80:20.

The compositions of the present invention are particularly suitable for ink jet printer inks, especially where the particulate solid is a pigment.

In the case of ink jet printing the composition according to the third aspect of the present invention preferably has a viscosity of less than 50mPa.s, more preferably less than 20mPa.s and especially less than 10mPa.s at a temperature of 25°C.

In the case of ink jet printing it is preferred that the composition according to the third aspect of the present invention preferably has a surface tension from 20 to 65 dynes/cm, more preferably from 25 to 50 dynes /cm.

The ink jet printing compositions of the present invention may also contain additional components conventionally used in ink jet printing inks, for example viscosity modifiers, pH buffers (e.g. 1:9 citric acid/sodium citrate) corrosion inhibitors, biocides, binders, dyes and kogation reducing additives.

According to a fourth aspect of the present invention there is provided a process for printing an image on a substrate comprising applying a composition according to the third aspect of the present invention to the substrate, preferably by means of an ink jet printer.

According to a fifth aspect of the present invention there is provided a paper, a plastic film or a textile material printed with a composition according to the third aspect of the present invention, preferably by means of an ink jet printer. Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character. Examples of commercially available papers include, HP Premium Coated Paper, HP Photopaper (all available from Hewlett Packard Inc.), Stylus Pro 720 dpi Coated Paper, Epson Photo Quality Glossy Film, Epson Photo Quality Glossy Paper (available from Seiko Epson Corp.), Canon HR 101 High Resolution Paper, Canon GP 201 Glossy Paper, Canon HG 101 High Gloss Film (all available from Canon Inc.), Wiggins Conqueror paper (available from Wiggins Teape Ltd), Xerox Acid Paper and Xerox Alkaline paper, Xerox Acid Paper (available from Xerox).

The plastic film may be opaque or transparent. Transparent plastic films which are suitable for use as overhead projector slides, include for example polyesters (especially polyethylene terephthalate), polycarbonates, polyimides, polystyrenes, polyether sulphones, cellulose diacetate and cellulose triacetate films.

According to a sixth aspect of the present invention there is provided an ink jet printer cartridge comprising a chamber and a composition according to the third aspect of the present invention wherein said composition is present in the chamber.

COATINGS AND PAINTS

Encapsulated particulate solids obtainable or obtained by the process of the present invention are particularly suitable for use in surface coatings and paints which comprise an encapsulated particulate solid, a liquid vehicle and a binder. The particulate solid is preferably a colorant or a filler. As with inks the paint can be made using the isolated encapsulated particulate solid but it is more preferred to use the composition comprising the encapsulated particulate solid and the liquid medium which results from the process according to the first aspect of the invention.

Thus according to an seventh aspect of the present invention there is provided a composition comprising an encapsulated particulate colorant or filler obtainable or obtained by a process according to the first aspect of the present invention, a binder and a liquid vehicle. The binder is a polymeric material capable of binding the composition on the volatilization of the liquid medium.

Suitable binders include natural and synthetic polymers. Preferred binders include poly(meth)acrylates, polystyrenics, polyesters, polyurethanes, alkyds, polysaccharides (e.g. cellulose) and proteins (e.g. casein). Preferably the binder is present in the composition at more than 100%, more preferably 200%, especially 300% and most preferably more than 400% based on the weight of the particulate solid.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

CLAIMS

1. A process for preparing an encapsulated particulate solid comprising cross-linking a poly vinyl dispersant with a cross-linking agent in the presence of a particulate solid and a liquid medium, thereby encapsulating the particulate solid within the cross-linked poly vinyl dispersant, characterised in that:

- a) the poly vinyl dispersant has a calculated Log P of less than 1.8 and at least one cross-linkable group; and
- b) the cross-linking agent is soluble in the liquid medium and has at least one cross-linking group.

2. A process according to claim 1 wherein poly vinyl dispersant has a calculated Log P of from 0 to 1.7.

3. A process according to any one of the preceding claims wherein the cross-linking is performed at a temperature of less than 60°C.

4. A process according to any one of the preceding claims wherein the resulting encapsulated particulate solid has a volume average particle size of at most 50% greater than the volume average particle size of the particulate solid prior to addition of the cross-linking agent.

5. A process according to any one of the preceding claims wherein the poly vinyl dispersant has an acid value of from 10 to 200mg KOH / g of dispersant.

6. A process according to any one of the preceding claims wherein the poly vinyl dispersant has at least one keto, aldehyde or beta-diketoester cross-linkable group.

7. A process according to claim 6 wherein the cross-linking agent has at least one amine, imine, hydrazide or thiol cross-linking group.

8. A process according to any one of the preceding claims wherein the resulting encapsulated particulate solid has a volume average particle size of at most 50% greater than the volume average particle size of the particulate solid prior to addition of the cross-linking agent.

9. A process according to any one of the preceding claims wherein the liquid medium comprises water.

10. A process according to any one of the preceding claims wherein the particulate solid is a pigment.

11. A process according to any one of the preceding claims comprising the further step of isolating the resultant encapsulated particulate solid from the liquid medium.

12. A process according to any one of the preceding claims wherein cross-linking is performed by mixing the following ingredients:

a) a liquid medium;

b) a particulate solid in a weight ratio of 1:100 to 1:3;

c) a poly vinyl dispersant in a weight ratio of 1:100 to 1:3.3; and

d) a cross-linking agent in a weight ratio of 1:10000 to 1:10;

wherein all weight ratios are relative to the weight of the liquid medium.

13. A process according to claim 12 wherein the liquid medium, the particulate solid and the poly vinyl dispersant are mixed and the mixture is subjected to a mechanical treatment to reduce the particle size of the particulate solid which is followed by the addition of the cross-linking agent to said mixture.

14. An encapsulated particulate solid obtainable by a process according to any one of the preceding claims.

15. A composition comprising a liquid vehicle and an encapsulated particulate solid according to claim 14.

16. A composition according to claim 15 having a viscosity of less than 20mPa.s at 25°C.

17. A composition according to claim 15 or 16 wherein the liquid vehicle comprises water and an organic solvent in a weight ratio of 99:1 to 5:95.

18. A process for printing an image on a substrate comprising applying a composition according to claim 15, 16 or 17 to the substrate.

19. A process according to claim 18 wherein the printing is performed by means of an ink jet printer.

20. A paper, a plastic film or a textile material printed with a composition according to claim 15, 16 or 17 by means of a process according to claim 18 or 19.

21. An ink jet printer cartridge comprising a chamber and a composition wherein the composition is present in the chamber and the composition is as claimed in claim 15, 16 or 17.

5 22. A composition according to claim 15 where the particulate solid is a colorant or a filler and the composition further comprises a binder.



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